J. Org. Chem. **1998,** *63,* 5368−5371

2-Biphenylenylcarbene[1]

Guoxian Wu and Maitland Jones, Jr.*

Department of Chemistry, Princeton University, Princeton New Jersey 08544

Richard Walton and Paul M. Lahti*

Department of Chemistry, University of Massachusetts at Amherst, Amherst, Massachusetts 01003

Received January 30, 1998

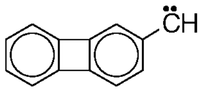
The reactivity and EPR spectroscopy of 2-biphenylenylcarbene have been examined. The reactive spin state is the singlet. The zero-field splitting parameters for the ground-state triplet approximate those of phenylcarbene.

Introduction

Many of the major themes of modern carbene chemistry have emerged during studies of arylcarbenes.[2] The interplay of singlet and triplet chemistry[3] and the determination of many absolute rates of reaction[3] were both important areas that found expression in this field. Naturally, phenylcarbene was the first species explored, and it was quickly determined that although the ground state was the triplet, much of its chemistry issued from the slightly higher energy (but *much* more reactive) singlet state.[2] However, phenyl diazomethane is hard to handle, and many workers chose to study 1- and 2-naphthylcarbene,[4] fluorenylidene,[5] and diphenylcarbene,[6] all available from more tractable precursors. In these two-ring carbenes[4−6] the ground state is again the triplet, but once more, much of the observed chemistry is derived from reactions of the singlet.

Helpful as these carbenes have been in the working out of arylcarbene chemistry, and they have been very useful, they do not quite cover all the available ground. Missing from the spectrum of two-ring aromatic carbenes (and all the others as well) is an example of an antiaromatic ring system interacting with divalent carbon. In this paper we describe some of the properties of such a system, biphenylenylcarbene **1**.

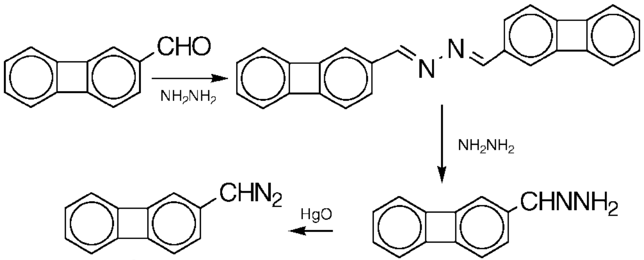
Of course, there are other test cases imaginable to probe the interaction between an antiaromatic ring system and a carbene, but they do not seem practicable at the moment. Cyclobutadienylcarbene would be ideal, and perhaps an antiaromatic annulene would have been a good candidate as well. But practical matters do intrude, and carbene **1** has one overwhelming advantage over other, prehaps better systems: it can be made. The price is that the biphenylene ring system is only weakly antiaromatic at best.[7] Nonetheless it seemed worthwhile to us to probe for unusual effects in this available, if not perfect molecule.



1

Synthesis of the Precursor

2-Formylbiphenylene was synthesized by a slight modification of published procedures.[8] Conversion into the azine was accomplished by treatment with anhydrous hydrazine. The azine was allowed to react with more anhydrous hydrazine to give the hydrazone, which could be isolated. Oxidation with yellow mercuric oxide led to the red-orange diazo coupound **2**, which was stable at refrigerator temperatures.



2

Results and Discussion

Irradiation of **2** in cyclohexane with a Pyrex-shielded 450 W Hanovia medium-pressure mercury arc led to a single product, which could be isolated by preparative thin-layer chromatography in 21% yield. Details of the spectra can be found in the Experimental Section, but a combination of high-resolution mass spectrometry, ^{1}H NMR spectroscopy, and ^{13}C NMR spectroscopy left no

---

[1] We thank the National Science Foundation for support of this work at Princeton through Grants NSF CHE-9322579 and CHE-9702823 and at Massachusetts through CHE-9521594.

[2] For a summary of arylcarbene chemistry, see: Wentrup, C. In *Methoden der Organische Chemie* (*Houben-Weyl*); Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 824−976.

[3] Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; Chapter 8.

[4] For an overview, see ref 3; for particular typical and thorough studies see: (a) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928 (1-naphthylcarbene). (b) Horn, K. A.; Chateauneuf, J. E. *Tetrahedron* **1985**, *41*, 1465 (2-naphthylcarbene).

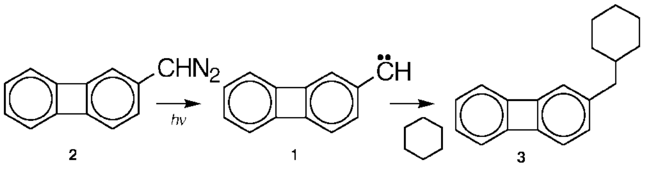
[5] For early product studies see: Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013. Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4015. For more recent spectroscopic work, see: Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

[6] Product studies: Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6286. Spectroscopic work: Eisenthal, K. B.; Turro, N. J.; Sitzman, E. V.; Gould, I. R.; Hefferon, J.; Lamgan, J.; Cha, Y. *Tetrahedron*, **1985**, *41*, 1543.

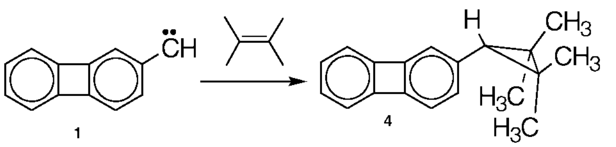
[7] Garratt, P. J. *Aromaticity*; Wiley: New York, 1986; p 234ff.

[8] Buckland, P. R.; McOmie, J. F. W. *Tetrahedron* **1977**, *33*, 1797.

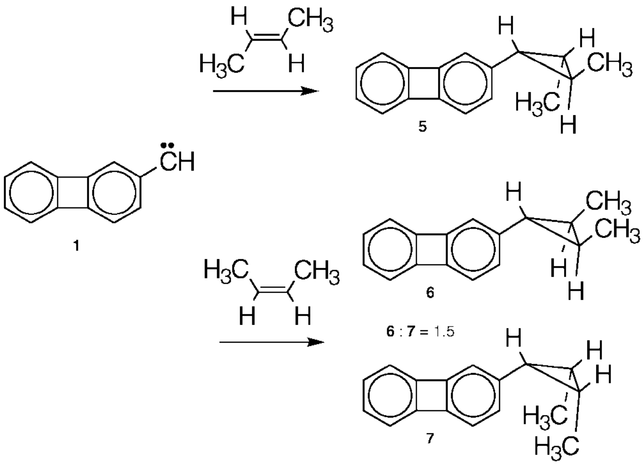
doubt as to the structure of the carbon−hydrogen insertion product, **3**. As bicyclohexyl was not a major product, it seemed likely that **3** was a result of a singlet insertion, rather than the abstraction−recombination process typical of triplet carbenes.[4a]



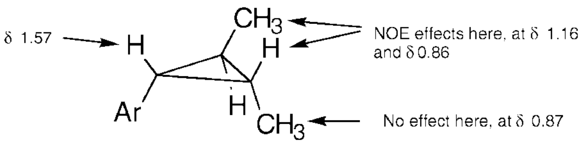
More definitively diagnostic for the reacting spin state would be an examination of the stereochemistry of addition to alkenes. We first verified that the addition process took place by adding carbene **1** to 2,3-dimethyl-2-butene. Once again a combination of spectroscopic techniques easily verified the anticipated structure, **4**, formed in 56% yield. Important points include the presence in the ^{1}H NMR spectrum of two 6H singlets (δ 0.96 and 1.2) and a single cyclopropane hydrogen at δ 1.37.



Now the question of the stereochemistry of addition arises. Irradiation of **2** in *trans*-2-butene led to a single cyclopropane adduct, **5**. *cis*-2-Butene led to a pair of adducts, **6** and **7**. In neither case was there significant (<ca. 1−2%) contamination by the “wrong” products.



Cyclopropane **5** is easily identified as the trans diastereomer as it is the only one of the three that shows two different methyl groups (δ 0.87 and 1.16). The methyl groups can be distinguished by an NOE experiment in which the benzylic hydrogen at δ 1.57 is irradiated. NOE effects are visible for the methyl group at δ 1.16 and the cyclopropyl hydrogen at δ 0.86, but not at the methyl group at δ 0.87. These data can now be used to assign the structures of the two cis cyclopropanes, each of which shows but a single methyl group. The one with a methyl signal at δ 1.14 must be the anti isomer, and the one with the methyl at δ 0.94 must be syn.



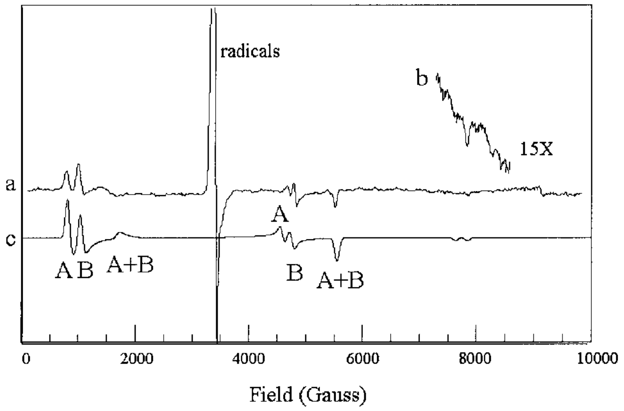
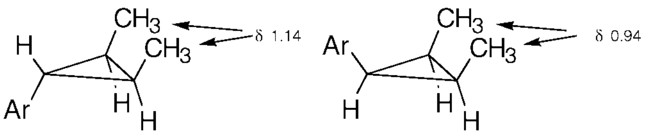


Figure 1. Experimental and simulated ESR spectra of **1**: curve a, 77 K 9.5 GHz spectrum of photolyzed **2** in methylcyclohexane; curve b ordinate expansion (15×) of curve a; curve c, simulated spectrum for 1:1 mixture of isomers of carbene **1** (see text for details).



Given these structural assignments, we can now work out the product ratios. Irradiation of **2** in *trans*-2-butene gives only **5**; irradiation in *cis*-2-butene gives **6** and **7** in a ratio of 1.5/1. At first sight, it may seem that there is “too much” of the syn adduct **7**. Not so. Phenylcarbene itself actually gives a slight excess of the syn adduct.[9] The source of this preference, whether couched in terms of molecular orbitals or resonance forms, is charge dispersal over the aromatic ring in the transition state for addition. With the methyl groups syn, favorable interactions overwhelm the steric problem. When charge dispersal in not present, as in carboranylcarbenes, the steric factors prevail.[10]

The overall pattern of reactivity thus resembles that of phenylcarbene, as addition is stereospecific. The singlet state is the reactive state.[11]

Although the reactive state is the singlet, there is no reason that the singlet must be the ground state of this carbene. As mentioned earlier, the two-ring arylcarbenes naphthylcarbene, fluorenylidene, and diphenylcarbene all have triplet ground states.[12] When **2** is irradiated at >300 nm (Pyrex filter, Xenon arc lamp) for 5 min at 77 K in degassed methylcyclohexane or 2-methyltetrahydrofuran glasses, the 9.5 GHz ESR spectrum shown in Figure 1 is obtained. The spectrum shows a strong peak at about $g \sim 2$ assigned to adventitious radicals,

---

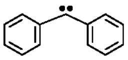
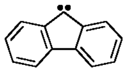
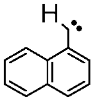
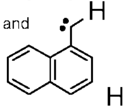
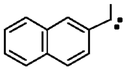
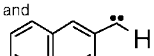
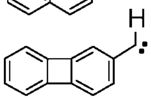
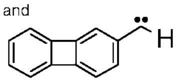
[9] Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. Gutsche, C. D.; Bachman, G. L.; Coffey, R. S. *Tetrahedron* **1962**, *18*, 617.

[10] Chari, S. L.; Chiang, S.-H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3138.

[11] A similar conclusion can be reached from a preliminary examination of the chemistry and spectroscopy of the 1-substituted biphenylenylcarbene. This system is harder to investigate than **1**, because starting materials are less stable, the syntheses are less efficient, and the separations of products are more difficult.

[12] Trozzolo, A, M. *Acc. Chem. Res.* **1968**, *1*, 329.

Table 1. Zero-Field Splitting Parameters for Some Arylcarbenes

Carbene	D/hc	E/hc	Reference[12]
	0.408	0.021	13
	0.407	0.027	14
 and 	0.435 0.456	0.021 0.020	15
 and 	0.493 0.471	0.021 0.024	15
 and 	0.422 0.403	0.025 0.020	this work

presumably derived by hydrogen-atom abstraction reactions between carbene and the solvent. Arylcarbenes, especially triplets, are known to be prone to hydrogen abstraction.[3] In addition, there are typical carbene peaks at 800 and 1000 G, a broad feature at 1300−1700 G, and rather sharper features at 4740, 4840, and 5500 G. This set of peaks is best reconciled with the presence of two geometric isomers of **1**, in a manner analogous to that previously observed for both 1- and 2-naphthylcarbenes, which give rise to the so-called cis and trans carbene isomers (Table 1).[3,4]

The zero field splitting (zfs) parameters for the two isomers of **1** were estimated by spectral line shape simulation using the eigenfield method.[18] The peaks at 800 and 4740 G were consistent with an S = 1 species (isomer A) having $|D/hc| = 0.403$ cm^{-1} and $|E/hc| = 0.025$ cm^{-1}. Those at 1000 and 4840 G were consistent with an S = 1 species (isomer B) having $|D/hc| = 0.422$ cm^{-1} and $|E/hc| = 0.020$ cm^{-1}. The peaks at about 1300−1700 G and at about 5500 G are common to both spectra. In addition, the simulations argue for the presence of high field peaks at about 7600 and 7800 G for isomers A and B, respectively. At very high signal gain, there is experimental evidence of very weak peaks in this spectral region (see curve b in Figure 1). A 1:1 summation of the simulations for isomers **1**-A plus **1**-B is a good match for the experimental spectrum when shown to scale in Figure 1, except for the radical peak in the experimental spectrum. Agreement between the observed and simulated peak positions is good to better than 10% where the peaks are strong enough to observe, and relative intensities are appropriate. As in earlier work by others on the naphthylcarbenes,[15] we are unable to assign the cis and trans isomers of the biphenylenylcarbenes to individual spectra.

In summary, carbene **1** appears to be a quite normal arylcarbene. Its reactivity approximates that of phenylcarbene, and although the zfs parameters for **1** do reveal slightly more delocalization than those for the naphthylcarbenes, the effect is not large.

Experimental Section

FTIR spectra were recorded with a Nicolet 730 spectrometer. ^{1}H and^{13}C NMR spectra were recorded with JEOL GSX-270, GE QE-300, and JEOL GSX-500 spectrometers. ^{1}H COSY and 1-D NOE experiments were conducted on a JEOL GSX-500 spectrometer. GC/MS analyses were carried out on a Hewlett-Packard 5890/5971 gas chromatograph equipped with a mass selective detector on a 0.25 mm i.d., 0.25 mm film thickness, 30 m HP-1701 capillary column. Precise masses were meansured on a KRATOS MS 50 RFA high-resolution mass spectrometer. Preparative gas chromatography was performed on a Gow-Mac series 580 gas chromatograph with a 10.5 ft × 1/4 in. 10% OV-101 on 80/100 Supelport column. The photolyses were conducted in Pyrex or quartz photolysis tubes irradiated by a 450 W medium-pressure Hanovia lamp. Melting points were determined on a Thomas-Hoover Uni-Melt appararus and are uncorrected.

2-Formylbiphenylene. 2-Formylbiphenylene was synthesized by a modification of the published procedure.[8] To a stirred solution of biphenylene (3.04 g, 0.02 mol) and dichloromethyl methyl ether (12.7 g, 0.11 mol) in 200 mL of ethylene dichloride chilled in an ice−water bath was injected 86.0 g of tin(IV) chloride under argon over a period of 2 min. When the addition was complete, the mixture was allowed to warm to room temprature and was stirred for 24 h. The mixture was then slowly poured with stirring into 300 mL of 3 M HCl cooled in a ice−water bath. The mixture was extracted with dichloromethane (3 × 100 mL) after it had stirred at room temperature for 1 h. The organic layers were combined and washed with 5% sodium bicarbonate solution (2 × 50 mL) and water (2 × 50 mL) and were dried over sodium sulfate. The solvent was removed on a rotary evaporator, and the residue was dissolved in benzene. The solution was filtered through a Büchner funnel with a layer of alumina. A yellow solution was collected by continuous washing with benzene. Removal of the benzene at the rotary evaporator gave 2-formylbiphenylene (3.1 g, 86%): mp 78−79 °C (lit.[8] mp 78−79 °C).

2-Formylbiphenylene Hydrazone. Anhydrous hydrazine (0.64 g, 0.02 mol) was added to the solution of 2-formylbiphenylene (1.8 g, 0.01 mol) in 30 mL of absolute ethanol. The flask was fitted with a condenser protected by a calcium chloride drying tube and heated under reflux for 20 h. On cooling in ice, yellow 2-formylbiphenylene azine separated and was recrystallized from ethanol. The product weighed 1.7 g (95%): mp 266−267 °C; IR 2905 (w), 1627 (m), 1414 (m), 1247 (m), 834 (m), 733 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.42 (s, 2H), 6.70−6.86 (m, 14H). HRMS *m/z* calcd for $C_{26}H_{16}N_2$ 356.13148, found 356.12936.

A mixture of 2-formylbiphenylene azine (1.0 g, 2.8 mmol), anhydrous hydrazine (0.45 g, 14.0 mmol), and 20 mL of

---

(13) Brandon, R. W.; Closs, G. L.; Hutchison, C. A. *J. Chem. Phys.* **1962**, *37*, 1878, Murray, R. W.; Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3213, Hutchison, C. A.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327.

(14) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990.

(15) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129.

(16) During the melting point determination bubbles evolved and the azine was formed.

(17) Miller, J. B. *J. Org. Chem.* **1959**, *24* 560.

(18) (a) Belford, G. G.; Belford, R. L.; Burkhalter, J. F. *J. Magn. Reson.* **1973**, *11*, 251. (b) Teki, Y.; Takui, T.; Yagi, H.; Itoh, K.; Iwamura, H. *J. Chem. Phys.* **1985**, *83*, 539. (c) Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134. (d) Teki, Y.; Fujita, I.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 11499. (e) Teki, Y., Ph.D. Thesis, Osaka City University, Osaka, Japan, 1985. (f) Details of the line shape program used by us are described in Sato, K. Ph.D. Thesis, Osaka City University, Osaka, Japan, 1994. We thank Prof. Sato for allowing us the use of this program.

absolute ethanol was heated under reflux for 10 h. Then the reaction mixture was concentrated by a rotary evaporator. A yellow solid was collected by filtration. Recrystallization of the product from ethanol gave 0.86 g of 2-formylbiphenylene hydrazone (80%): mp 193−195 °C;[16] IR 3361 (m), 2906 (w), 1566 (m), 1442 (m), 1369 (m), 1124(m), 920 (s), 829 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (s, 1H), 6.60−6.79 (m, 7H), 5.46 (s, 2H).

2-Diazomethylbiphenylene. The method of Miller[17] was adapted to the synthesis of 2-diazomethylbiphenylene. In a pressure bottle wrapped in a wet towel, a mixture of 0.80 g of 2-formylbiphenylene hydrazone (4.4 mmol), 0.9 g of sodium sulfate, 15 mL of anhydrous ether, 15 drops of a freshly made saturated solution of potassium hydroxide in ethanol, and 2.0 g of yellow mercuric oxide was shaken for 90 min. The reaction mixture was filtered through a Hirsch funnel, and 10 mL of hexane was used to wash the solid. The filtrate was collected and concentrated under reduced pressure at the water pump. The orange residue obtained was dissolved in hexane and filtered again. After the hexane was removed, the residue was placed in a refrigrator and gave 0.32 g of red solid (41%): IR 3074 (w), 2050 (m), 1442 (w), 1100 (w), 817 (m), 731 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.29 (s, 1H), 6.54−6.76 (m, 7H).

Photolysis of 2-Diazomethylbiphenylene in Cyclohexane. A solution of 15.2 mg of 2-diazomethylbiphenylene in 10 mL of cyclohexane was prepared. The solution was transferred to a quartz photolysis tube, degassed by the freeze−thaw method, and irradiated for 2 h. The reaction mixture was then transferred to a vial. The photolysis tube was washed with dichloromethane, and all the organic solutions were combined. A sample of 4.0 mg of 2-cyclohexylmethylbiphenylene was obtained by prepative TLC (20.6%): ^{1}H NMR ($CDCl_3$) δ 6.49−6.73 (m, 7H), 2.28 (d, 2H, J = 7 Hz), 0.93−1.72 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 128.33, 127.98, 119.19, 117.31, 117.25, 117.07, 44.85, 39.73, 33.32, 26.78, 26.55; HRMS m/z calcd for $C_{19}H_{20}$ 248.15660, found 248.15578.

Photolysis of 2-Diazomethylbiphenylene in 2,3-Dimethyl-2-butene. A sample of 15.0 mg of 2-diazomethylbiphenylene was dissoved in 5 mL of 2,3-dimethyl-2-butene. The solution was transferred to a quartz photolysis tube, degassed by the freeze−thaw method, and irradiated for 2 h. Then, the reaction mixture was transferred to a vial. The photolysis tube was washed with dichloromethane, and all the organic solutions were combined. A sample of 10.8 mg of cyclopropane **4** was obtained by prepative TLC (55.7%): ^{1}H NMR ($CDCl_3$) δ 6.46−6.72 (m, 7H), 1.37 (s, 1H), 1.21 (s, 6H), 0.97 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 130.73, 128.76, 128.48, 121.48, 117.77, 117.59, 38.93, 24.47, 19.72; HRMS m/z calcd for $C_{19}H_{20}$ 248.15660, found 248.15672.

Photolysis of 2-Diazomethylbiphenylene in *trans*-2-Butene. 2-Diazomethylbiphenylene was transferred to a quartz photolysis tube fitted with a T-joint closed by a high-vacuum stopcock. *trans*-2-Butene (5 mL) was introduced into the tube while the tube was chilled in a liquid nitrogen bath. The solution was degassed by three cycles of the freeze−thaw method. Then the photolysis tube was immersed in a water bath and irradiated for 2 h. Cyclopropane **5** was separated by preparative TLC and purified by preparative gas chromatography: ^{1}H NMR ($CDCl_3$) δ 6.51−6.72 (m, 7H), 1.57 (dd, 1H, J = 5.37, 8.06 Hz), 1.16 (d, 3H, J = 5.37 Hz), 0.87 (d, 3H, J = 5.37 Hz), 0.86 (m, 1H), 0.84 (m, 1H); HRMS m/z calcd for $C_{17}H_{16}$ 220.12528, found 220.12508.

Photolysis of 2-Diazomethylbiphenylene in *cis*-2-Butene. The reaction was carried out in a manner similar to that described above for *trans*-2-butene. Two products, **6** and **7**, were separated by preparative gas chromatography. **6**: ^{1}H NMR ($CDCl_3$) δ 6.53−6.72 (m, 7H), 1.82 (t, 1H, J = 8.57), 1.13 (m, 2H), 0.94 (d, 6H, J = 5.93); HRMS calcd 220.12528, found 220.12455. **7**: ^{1}H NMR ($CDCl_3$) δ (ppm) 6.52−6.78 (m, 7H), 1.14 (d, 6H, J = 4.27 Hz), 1.02 (t, 1H, J = 4.28 Hz), 0.89 (m, 2H); HRMS m/z calcd for $C_{17}H_{16}$ 220.12528, found 220.12455.

JO980169J